FUNDAMENTAL TRANSITION IN THE ELECTRONIC NATURE OF SOLIDS*

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(Received 6 March 1969)

Striking evidence for a fundamental covalent-ionic transition in the electronic nature of solids is presented.

The fundamental electronic properties of nonmetallic, inorganic, crystalline solids depend in a natural manner on the character of the chemical bond which is developed between constituent atoms. For example, the familiar Group-IV semiconductors are totally covalent and exhibit characteristics which are qualitatively different from highly ionic materials, such as the alkali halides. However, many materials of fundamental and practical importance are intermediate between these two extremes; it is not immediately evident how their properties may be treated. We will demonstrate here that if crystalline solids are ordered by some measure of their bond ionicity, then one finds striking evidence for a universal and surprisingly abrupt transition in many electronic properties associated with the quantum mechanical valence state. This transition divides crystalline solids into two well-defined classes: "covalent" and "ionic." Within each class there is a unifying character to the observed properties.

The first systematic treatment of the partial ionic character of chemical bonds was given by Pauling.[1] Over the range of materials we discuss, the difference in electronegativity (X) of the two constituents of a binary compound gives a crude but monotonic measure of the ionicity of the compound. Although improved methods for characterizing the ionicity of compounds have been proposed,[2] the nature of the transition under discussion here is not materially dependent upon which ionicity scale is used and for convenience we will use the electronegativity difference ΔX.

It has been generally recognized for some years that semiconductors can be classified into two broad groups based on the properties of the semiconductor-metal interface.[3,4] "Ionic" materials display little or no Fermi-level stabilization at the interface; "covalent" materials display virtually complete stabilization. The classic experiment consists of measuring the barrier energy at the metal-semiconductor interface as a function of the electronegativity X_M of the metal employed. Typical results[5,6] are shown in Fig. 1 for SiO_2 and vacuum-cleaved Si. The slope $S = (d\Phi_{Bn}/dX_M)$ of a straight line fitted to the data is inversely correlated to the extent of Fermi-level stabilization. This slope is found to be $\simeq 1$ (no Fermi-level stabilization) for "ionic" materials and $\simeq 0.1$ (nearly complete Fermi-level stabilization) for "covalent" materials. Recent data[7] obtained for the layer compound GaSe are also shown in Fig. 1; this material displays partial Fermi-level stabilization, $S \simeq 0.6$. Experiments on the isostructural layer compounds GaS and GaTe reveal[8] that this result is not a consequence of the layer structure, but appears to be related to a continuous transition from the "ionic" properties of GaS to the "covalent" properties of GaTe. A similar, although less well-defined, transition has been observed in the CdS_xSe_{1-x} mixed-crystal system.[4] These results suggest that the covalent-ionic transition may be elucidated by plotting slope S as a function of ΔX. Such a plot is shown as Fig. 2(a). There is evidently a well-defined transition between the interface properties of "ionic" materials and those of "covalent" materials.

Lattice termination is a severe disruption of

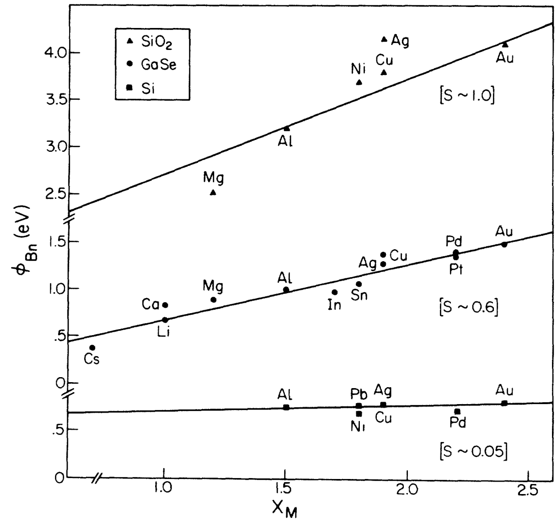

FIG. 1. Barrier energies of various metals on *n*-type semiconductors plotted versus electronegativity X_M of the metal. For each material, slope S of the reference line is inversely proportional to the extent of Fermi-level stabilization at the semiconductor-metal interface.

crystalline perfection and hence one would expect a large perturbation of valence-state energy at the surface of a solid. However, the data presented above indicate that this large perturbation occurs only for covalent materials. A simple Madelung calculation for highly ionic solids reveals that the electrostatic contribution to the binding energy for an atom at the surface is virtually identical to that for an atom in the bulk.[9] This result emphasizes the nonuniqueness of the surface in an ionic solid (i.e., there is virtually no energy differential for an atom at the surface; a lack of states at a given energy in the bulk would thus imply a lack of states of the same energy at the surface). On the basis of such elementary considerations we are led to the possibility that in "ionic" crystals effects attributable to long-range order may not dominate the observed properties (see also McGill, Kurtin, and Mead[10]).

If the transition displayed in Fig. 2(a) is fundamental to the nature of electron states in solids, it should be evident not only in phenomena involving lattice termination, but also in totally independent experiments, as for example in photoemission studies. Spicer et al.[11] have used energy analysis of photoemitted electrons to study photon-induced electronic transitions in a wide variety of solids. These experiments allow an assessment of the relative importance in a given solid of the different types of optical transitions: "direct" (single-particle crystal momentum *k* is conserved, "nondirect" (single-particle *k* conservation is not an important selection rule), and "indirect" (single-particle *k* is conserved with phonon participation). Of course, in all cases total momentum is conserved; however, in many materials nondirect transitions dominate the observed optical excitations. In Fig. 2(b) we plot the relative importance of nondirect transitions as a function of ΔX for many solids.[12] The similarity between Figs. 2(a) and 2(b) strongly suggests that the covalent-ionic transition is directly related to conservation of crystal momentum in optical excitations.

To summarize, the electronic valence states

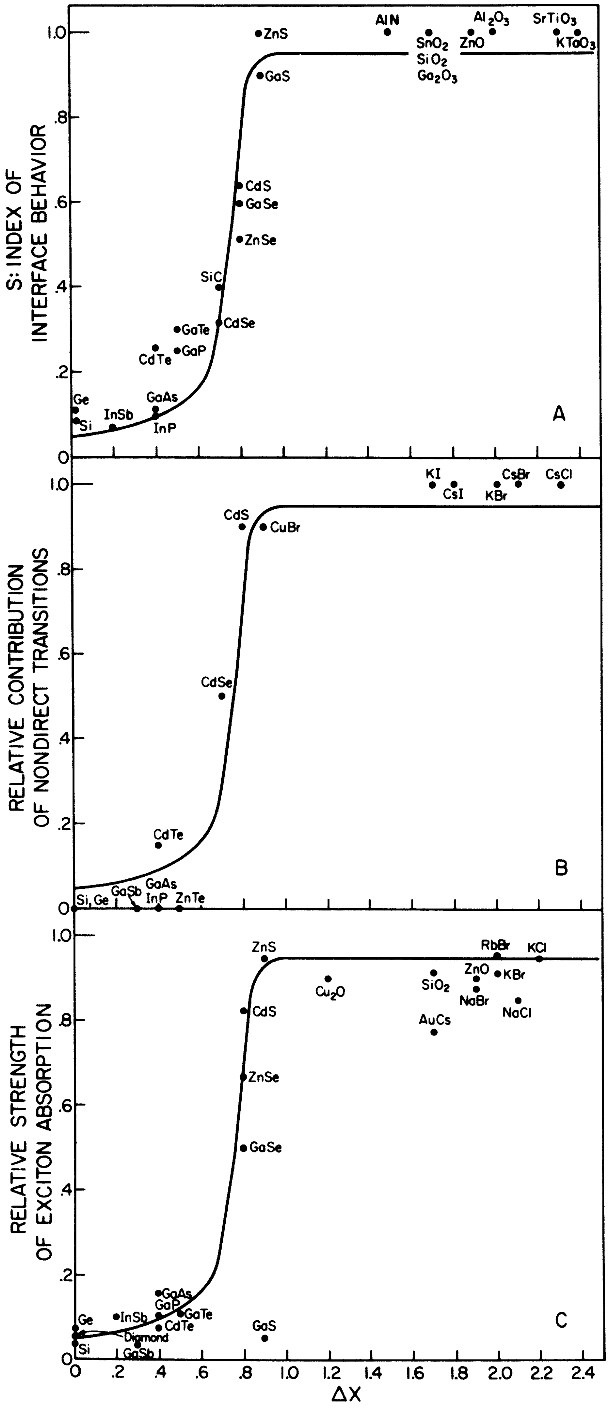

FIG. 2. Collected data representing several independent experiments plotted as a function of lattice electronegativity difference ΔX. (a) The slope S obtained from plots similar to Fig. 1; S is inversely proportional to the Fermi-level stabilization at the semiconductor-metal interface. (b) The relative contribution of nondirect transition in photon induced electronic excitations, as measured by photoemission studies. (c) The relative strength of exciton absorption as determined from optical spectra. These three independent experiments all illustrate the fundamental covalent-ionic transition in solids. (Details of the compilation of these data although straightforward are too lengthy to appear here. They will be discussed in detail in Ref. 10.) The same arbitrary curve is shown in all three sections of this figure for illustrative purposes.

of covalent materials are appropriately described in terms of an independent-particle k and lattice termination leads to a significant perturbation of electron energy near the surface (a large density of surface states). These observations are consistent with the simplified but historically significant treatment of surface states by Shockley.[13] In contrast, ionic materials ($\Delta X \gtrsim 0.9$) are characterized by the absence of k conservation in optical transitions and by a small density of surface states ($<10^{11}/\mathrm{cm}^2$). Lack of single-particle k conservation, which occurs solely in the more ionic crystals, may be viewed as a result of localization of valence electronic wave functions; i.e., the spatial coordinates $\vec{r}$ become a more appropriate basis for describing electronic valence states than momentum coordinates $\vec{k}$.

The fundamental nature of the covalent-ionic transition in solids may be further illustrated by examining its influence on optical spectra in the neighborhood of the absorption edge. "Ionic" materials exhibit large absorption peaks near the edge, a consequence of localized excitons. Even at extremely low temperature, "covalent" materials show a smooth onset of absorption with only a very small peak. The extent to which the exciton peak dominates the absorption edge can be estimated from the ratio of the area of the peak itself to the total area of the peak plus general background under the peak. The relative strength of the exciton peak was determined in this manner from published optical spectra[14] on a number of materials and is plotted versus ΔX in Fig. 2(c). Although these data are the result of an experiment quite different from those previously discussed the covalent-ionic transition is once again very much in evidence.

Several independent types of experiments have been discussed. These experiments were chosen because they bear directly on the nature of the electronic valence state, and because they have been performed on a wide variety of materials and crystal structures. Strong evidence of the fundamental transition is also seen in many other phenomena involving electronic properties associated with valence states in solids.[12]

From a theoretical point of view, the overwhelming complexity of a realistic solution to the many-body problem in solids has necessitated the development of single-particle-like approximations. Since the procedure for obtaining independent-particle approximations is not unique, physically meaningful approximations are best motivated by experimental evidence. In the covalent limit a band approximation based on extended Bloch-like valence states has met with great success. In principle, "ionic" materials may be treated by starting with the band approximation and including correlation effects as a perturbation. However, the experimentally observed properties of "ionic" crystals indicate that an independent-particle approximation based on localized valence states may be more appropriate for these materials. In fact, the very abruptness of this transition implies that any attempt to describe "ionic" solids by the inclusion of electron-electron correlation as a perturbation upon delocalized valence states will be extremely involved since it is necessary to change the *character* of the initially assumed states. We believe that the experimental evidence indicates that localized valence states provide a more appropriate (and conceptually correct) basis from which refined treatments of "ionic" materials may be developed.

The authors would like to thank R. P. Feynman, J. M. Ziman, K. K. Thornber, W. A. Goddard, III, and J. Bardeen for much helpful discussion, and J. C. Phillips for supplying preprints of his recent work. The cooperation of W. E. Spicer, without which this paper would have suffered immeasurably, is deeply appreciated.

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*Work supported in part by the Office of Naval Research.

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[9] $\alpha_b \equiv \sum_j (\pm 1/P_{ij}) = 1.748$ for an atom in the bulk of an fcc structure; $\alpha_s \equiv \sum_j (\pm 1/P_{ij}) = 1.682$ for an atom at the surface of a terminated 3-D array with the same structure. Therefore, on the basis of this model there is an energy shift at the surface of less than 4%.

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[12] The authors are deeply indebted to W. Spicer for providing much unpublished data and for assessing the relative importance of nondirect transitions in these materials.

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MAGNETOSTRICTION AND ANOMALOUS THERMAL EXPANSION OF CHROMIUM

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(Received 28 April 1969)

Crystal distortions in Cr associated with antiferromagnetic ordering have been established using electrical-resistance strain gauges. Between 123 and 311°K the observations confirm the existence of an orthorhombic structure associated with the presence of a transversely polarized spin-density wave.

The antiferromagnetism of chromium is now well established.[1-11] The Néel temperature T_N is 311°K, below which the antiferromagnetic state is that of a spin-density wave (SDW). In the so called AF$_1$ phase, between 123 and 311°K, the polarization is perpendicular to the wave vector of the SDW; below 123°K the polarization and wave vectors are parallel. This longitudinally polarized phase (LSDW) is conventionally known as the AF$_2$ phase. The transition between the two phases is first order and is often described by the term "spin flip" (T_{SF} = 123°K). In the transversely polarized AF$_1$ phase (TSDW) the wave vector is a continuous function of temperature[3-5,11] and at T_N the phase transition to the paramagnetic state is also first order.[11]

The AF$_1$ phase exhibits marked elastic anomalies and magnetoelastic effects.[12-14] In particular the polycrystalline Young's modulus is anomalously low[12] and the distribution of SDW's among the six otherwise equivalent (100) directions is drastically affected by cooling a sample through T_N in the presence of either an external magnetic field[9,13-20] or a uniaxial stress.[9,20]

Many workers[6,7,11,14,16,18] have pointed out that the magnetic symmetry of the antiferromagnetic states is inconsistent with the retention of full cubic symmetry. The AF$_2$ state will, in general be tetragonal and the AF$_1$ state orthorhombic. It is generally agreed[13] that the loss of cubic symmetry would account, in principle, for both the stress-cooling and elastic-constant behavior. The former would have its origin in a macroscopic distortion parallel to the wave vector of the SDW. A lattice distortion associated with direction of the polarization vector of SDW would account for the latter since an elastic stress could remove the degeneracy associated with the otherwise equivalent two directions of polarization. The removal of the degeneracy is supposed to take place by the motion of antiferromagnetic domain walls separating two transversely polarized SDW's of the same wave vector. This mechanism could explain the observation that a large magnetic field reduces the elastic anomaly[14] since a magnetic field can induce wall movement, ultimately to a degree at which further stress-induced wall movement cannot occur.

Unfortunately, attempts to detect these lattice distortions have, so far, been unsuccessful.[11,21,22] The most ambitious of these to date[22] established that the lattice distortion is certainly less than 10^{-5}. Refined x-ray techniques capable of detecting distortions at least an order of magnitude smaller than this certainly exist but they are applicable only to materials more structurally perfect than polycrystalline or single-crystal metals and moreover are limited to investigations at or near ambient temperatures. It seems likely, therefore, that the distortions which are being sought are below the limits of sensitivity of presently applicable x-ray techniques.

We have succeeded in detecting the anticipated lattice distortions using standard magnetostriction techniques. Measurements were made on a single crystal of chromium in the form of a disk with a [001] plane in its plane. The crystal was annealed according to the recipe of Street.[12] Low-magnetoresistance strain gauges were fixed along the [010] direction and the strain was observed when a magnetic field of 25 kOe was rotated from the [100] direction to the [010] direc-